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EFFECT OF TIME OF DIGESTION ON THE HYDROLYSIS OF CASEIN IN THE PRESENCE OF STARCH[1]

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The Van Slyke[2] method for protein analysis was worked out upon mixtures of relatively pure amino acids and was not intended to be applied directly to crude sources of protein contained in cereals and feeding stuffs.

Notwithstanding this fact, Grindley, Slater, et al.,[3] of the Illinois Experiment Station, published in 1915 the results of the determination of the amino acids contained in cottonseed meal, tankage, and alfalfa hay, applying the Van Slyke method directly to the proteins contained in these different feeds.

In the same month of 1915 Nollau,[4] of this Station, published his results, obtained by the Van Slyke method, on about 25 different sources of crude protein contained in various seeds and feeding stuffs.

In December, 1915, Grindley, Slater, et al.,[3] published a second paper on the amino-acid content of various feeds, including wheat, oats, barley, and sov beans, a number of which had been analyzed by Nollau. The summary of their second paper in part is as follows:

> The results here reported confirm the conclusion previously drawn, namely, that the Van Slyke method for the determination of the chemical groups characteristic of the amino acids of proteins can be applied directly to the quantitative determinations of the amino acids of feeding stuffs with at least a fair degree of accuracy.
>
> The results which we have obtained for the quantitative determinations of amino acids in feeding stuffs, on the whole, do not agree well with those recently published by Nollau. In some determinations the results from the two sources are quite satisfactory, but in many cases the agreement is far from satisfactory. The lack of con-

[1] Approved for publication in the Journal of Agricultural Research by A. M. Peter, Acting Director, Kentucky Agricultural Experiment Station.

[2] VAN SLYKE, D. D. THE ANALYSIS OF PROTEINS BY DETERMINATION OF THE CHEMICAL GROUPS CHARACTERISTIC OF THE DIFFERENT AMINO ACIDS. *In* Jour. Biol. Chem., v. 10, no. 1, p. 15–55, 2 fig. 1911.

[3] GRINDLEY, H. S., SLATER, M. E., et al. THE QUANTITATIVE DETERMINATION OF THE AMINO ACIDS OF FEEDING STUFFS BY THE VAN SLYKE METHOD. *In* Jour. Amer. Chem. Soc., v. 37, no. 7, p. 1778–1781; no. 12, p. 2762–2769. 1915.

[4] NOLLAU, E. H. THE AMINO-ACID CONTENT OF CERTAIN COMMERCIAL FEEDING STUFFS AND OTHER SOURCES OF PROTEIN. *In* Jour. Biol. Chem., v. 21, no. 3, p. 611–614. 1915.

cordant results is probably due in the main to differences in the details of procedure in the experimental work.

Hart and Bentley,[1] of the Wisconsin Experiment Station, comment unfavorably on the lack of agreement between the results obtained by Grindley, Slater, et al., and those obtained by Nollau for the amount of the different amino-acid groups contained in feeding stuffs. They state that whether accurate determinations of any or all the amino acids can be secured when the hydrolyzing proteins are in contact with hydrolyzing carbohydrates must first be determined before these data can be accepted as final.

Presumably in order to substantiate the theory in regard to the effect of hydrolyzing carbohydrates on the different amino-acid groups in proteins, Hart and Sure [2] have published results obtained upon the hydrolysis of casein, alone and in the presence of a number of different carbohydrates. In one of their experiments, 2.4 gm. of casein and 12 gm. of starch were hydrolyzed by boiling in 20 per cent hydrochloric acid for a period of 48 hours. The result obtained for lysin in this experiment shows that approximately 50 per cent of this amino-acid group has been changed to some other form of combination. They summarize their results in part as follows:

> The Van Slyke method of protein analysis, applied to casein, hydrolyzed in the presence of various carbohydrates, brings about a total redistribution of the amino-acids varying with the nature of the carbohydrate employed. This work on casein and Gortner's work on fibrin, hydrolyzed in the presence of cellulose, *definitely* show the inapplicability of the method of direct hydrolysis for the estimation of amino-acids in feeding stuffs by Van Slyke's method. The results so secured will be inaccurate.

Upon the publication of Hart and Sure's results, it appeared to the writer that their conclusions were much broader than their experiments justified. In fact, Hart and Bentley [3] make statements which appear to be merely forecastings rather than conclusions arrived at by experimentation. In order to be able to say positively that the Van Slyke method for protein analysis can not be applied directly to heterogeneous mixtures of protein and carbohydrate requires much further experimentation. It is by no means to be taken for granted that results obtained on a 48-hour digestion will be the same as those carried on for a shorter length of time.

It therefore occurred to the writer that a duplication of the experiment of Hart and Sure upon the effect produced on the hydrolysis of casein by the presence of starch, in which the time of digestion varied, would afford more conclusive evidence on this subject. Accordingly, five experiments were planned, as follows:

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[1] HART, E. B., and BENTLEY, W. H. THE CHARACTER OF THE WATER-SOLUBLE NITROGEN OF SOME COMMON FEEDING STUFFS. *In* Jour. Biol. Chem., v. 22, no. 3, p. 477-483. 1915.

[2] ..... and SURE, Barnett. THE INFLUENCE OF CARBOHYDRATES ON THE ACCURACY OF THE VAN SLYKE METHOD IN THE HYDROLYSIS OF CASEIN. *In* Jour. Biol. Chem., v. 28, no. 1, p. 241-249. 1916.

[3] HART, E. B., and BENTLEY, W. H. Op. cit.

Five 10-gm. portions of Hammarsten's casein were weighed out and transferred to five 1-liter round-bottom Jena flasks. Fifty gm. of cornstarch were then weighed out and added to each of the flasks except the first, which contained casein alone. Three hundred c. c. of 20 per cent hydrochloric acid, specific gravity 1.11, were added to each flask. All the flasks were then heated on the water bath, with frequent shakings, for about two hours. The object of this preliminary heating on the water bath was to liquefy the starch-casein mixtures, which had gelatinized upon the addition of the hydrochloric acid. After the starch had become liquid all the flasks were removed and attached to reflux condensers and heated to a gentle boil.

Experiments 1 and 2 were allowed to digest for 12 hours, No. 3 for 15 hours, No. 4 for 24 hours, and No. 5 for 48 hours, each being cut out at the expiration of its time interval.

After each of the experiments had stood at room temperature for six or eight hours, they were filtered through paper on a Buchner funnel and washed practically free of chlorids with hot water. There was no insoluble residue remaining on the filter from the casein digestion. There were rather large insoluble carbonaceous residues remaining from each of the casein-starch mixtures. Each of these was dried at 100° C., bottled, and set aside for further investigation as to their nitrogen content.

The filtrates in each of the experiments were concentrated separately under reduced pressure until practically all of the excess of hydrochloric acid was removed. The residues were taken up in water and run through filters into separate flasks of 250-c. c. capacity. After the filters were washed thoroughly, the contents of each flask were brought up to the mark with water, and duplicate analyses were carried out by the Van Slyke method on aliquots from each of these hydrolyzed solutions. The results obtained are shown in Table I.

From the data in Table I showing the average results obtained upon casein alone and upon definite mixtures of starch and casein digested at different intervals of time the following observations may be made.

In all of the experiments there is but slight variation in the ammonia determinations[1]; the maximum result is obtained in the 48-hour digestion. The increase in this case is in all probability owing to the change of some of the amino groups to ammonia compounds, which indicates over-digestion.

The results for the humin determinations show a diminution in the 15-, 24-, and 48-hour digestions over those of the 12-hour digestions. However, the humin determination in the 12-hour digestion of the starch-casein mixture agrees well with the humin results obtained on casein alone.

[1] Previous to the ammonia determinations the acidity of the hydrolyte, in terms of the calcium-hydrate suspension, was determined by titration, with phenolphthalein as the indicator. A slight excess of the calcium-hydrate suspension above the amount necessary to neutralize the acid was always added.

TABLE I.—*Effect produced upon the hydrolysis of casein in the presence of starch by varying the time of digestion*

Amino-acid group.	Experiment 1 (10 gm. of casein+300 c. c. of 20 per cent hydrochloric acid; boiled for 12 hours).			Experiment 2 (10 gm. of casein+50 gm. of cornstarch+300 c. c. of 20 per cent hydrochloric acid; boiled for 12 hours).			Experiment 3 (10 gm. of casein+50 gm. of cornstarch+300 c. c. of 20 per cent hydrochloric acid; boiled for 15 hours).			Experiment 4 (10 gm. of casein+50 gm. of cornstarch+300 c. c. of 20 per cent hydrochloric acid; boiled for 24 hours).			Experiment 5 (10 gm. of casein+50 gm. of cornstarch+300 c. c. of 20 per cent hydrochloric acid; boiled for 48 hours).		
	No. 1	No. 2.	Average.	No. 1.	No. 2.	Average.	No. 1.	No. 2.	Average.	No. 1.	No. 2.	Average.	No. 1.	No. 2.	Average.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Ammonia nitrogen	10. 20	10. 29	10. 24	10. 31	10. 21	10. 26	9. 46	10. 28	9. 87	10. 09	10. 01	10. 05	11. 29	10. 90	11. 10
Humin nitrogen	1. 32	1. 32	1. 32	1. 47	1. 47	1. 47	1. 10	.75	.92	.95	.95	.95	.74	.80	.77
Arginin nitrogen	7. 99	7. 90	7. 94	6. 49	7. 06	6. 77	5. 46	6. 21	5. 83	6. 32	6. 23	6. 27	6. 00	6. 00	6. 00
Histidin nitrogen	7. 94	8. 15	8. 04	8. 18	8. 18	8. 18	6. 93	5. 90	6. 41	1. 19	1. 79	1. 49	2. 71	2. 59	2. 65
Cystin nitrogen	.14	.17	.15	.19	.16	.17	.15	.19	.17	.07	.06	.07	.07	.05	.06
Lysin nitrogen	9. 13	9. 50	9. 31	8. 79	8. 82	8. 80	8. 03	9. 47	8. 75	10. 37	9. 85	10. 11	11. 58	9. 88	10. 73
Amino nitrogen in filtrate from bases	57. 38	57. 19	57. 28	58. 06	56. 90	57. 48	57. 60	57. 79	57. 69	59. 14	58. 31	58. 72	56. 97	56. 94	56. 95
Nonamino nitrogen in filtrate from bases	8. 67	8. 26	8. 46	8. 47	10. 31	9. 36	11. 15	8. 93	10. 04	8. 80	10. 17	9. 48	8. 37	9. 69	9. 03
Total	102. 77	102. 78	102. 74	101. 96	103. 11	102. 52	99. 88	99. 52	99. 68	97. 03	97. 47	97. 25	97. 73	96. 85	97. 29

The results on humin represent the humin in solution and precipitated by calcium-hydrate suspension. The high results obtained by Grindley, Slater, et al. and Hart and Sure for humin nitrogen were made to include the total nitrogen in the insoluble residue and also the humin in solution.

It has been the experience of the writer that in cases where considerable insoluble residue was included in the total volume of the hydrolyte, great difficulty was met with in obtaining uniform aliquots for the total nitrogen in the solution and also for the aliquot for determination. This difficulty is avoided by filtering out and washing the insoluble residue. Then, too, the question arises, Is it fair to consider the nitrogen remaining in the insoluble residue as humin nitrogen?

The results for arginin show no serious loss in any of the determinations, and the minimum result obtained is only 1.5 per cent below Van Slyke's result for arginin on casein alone.

The histidin results are practically the same for the two 12-hour digestions, on casein alone and on the casein-starch mixture. In the 15-hour casein-starch digestion the result for histidin is 0.61 per cent above that reported in Van Slyke's analysis. In the 24- and 48-hour digestions there is a loss in histidin nitrogen of considerably more than 50 per cent of that found in the 15-hour digestion. Hence, the results for histidin in the two last experiments are very significant, indicating that long periods of digestion of starch and casein bring about a redistribution of the nitrogen in this group. It is to be borne in mind that Hart and Sure[1] obtained similar results on lysin. These writers also report 7.30 per cent as a average for histidin determinations in their experiment.

There is a diminution in the cystin nitrogen of more than 50 per cent in the 24- and 48-hour digestions. Hart and Sure state that their results for cystin were so low that they reported the results obtained by Van Slyke instead.

The results for lysin agree well in the 12- and 15-hour experiments. In the 24- and 48-hour experiments the results for lysin are high. Lysin nitrogen is obtained by deducting the sum of histidin, arginin, and cystin nitrogen from the total nitrogen in the bases; therefore any diminution in the nitrogen content of either histidin, arginin, or cystin will increase the results for lysin nitrogen correspondingly.

There is no marked difference between the results obtained in all the experiments for the amino- and nonamino-nitrogen content in the filtrates from the bases.

In the footings of the different analyses it is to be noted that the 12-hour digestions give footings more than 2.5 per cent over 100. In the 15-hour digestion the footing is good, while in the 24- and 48-hour digestions the footings are 2.75 per cent less than 100, thus indicating that the 12-hour experiments were probably not completely hydrolyzed;

[1] HART, E. B., and SURE, Barnett. Op. cit.

whereas the 15-hour digestion was sufficient to bring about complete hydrolysis and the 24- and 48-hour experiments were overdigested to the extent that nitrogen was lost.

The insoluble carbonaceous residues which were filtered from the hydrolyzed solutions were dried at 100° C. and the total nitrogen determined in each.

The insoluble residue from experiment 2, or the 12-hour starch-casein digestion, contained 1.30 per cent of nitrogen. That from the 15-hour digestion contained 0.83 per cent of nitrogen. That from the 24-hour digestion contained 0.80 per cent of nitrogen and that from the 48-hour digestion contained 0.855 per cent of nitrogen. The results show that a 15-hour digestion removed as much nitrogen from the insoluble residue as the 24- and 48-hour digestions.

Two determinations of total nitrogen on a sample of the dry starch showed an average nitrogen content of 0.05 per cent. The small amount of nitrogen contained in the starch and the comparatively greater amount found in the insoluble residues indicate that some nitrogen compound was absorbed by the latter.

Seven gm. of the dry-carbon residue were weighed out and transferred to a Claisen flask, 60 c. c. of a 10 per cent calcium-hydrate suspension added, together with 250 c. c. of distilled water. The apparatus was connected up as in an ammonia determination and distilled under reduced pressure at from 40° to 45° C. for 30 minutes. Nine-tenths c. c. of *N/10* hydrochloric acid was neutralized by the ammonia evolved, which shows that the insoluble-carbon residue contained only a trace of ammonia nitrogen. The insoluble-carbon and calcium-hydrate precipitate remaining in the Claisen flask was filtered and washed thoroughly, the filtrate made acid and concentrated under reduced pressure to about 50 c. c. The concentrate was transferred to a Kjeldahl flask and the total nitrogen determined in the usual way. The filtrate contained 0.0032 gm. of nitrogen or 5.3 per cent of the total nitrogen contained in the insoluble residue. The ammonia nitrogen was 2.1 per cent of the total nitrogen in the carbon residue. It is therefore evident that a very small percentage of the total nitrogen contained in the insoluble residue is affected by distilling with calcium-hydrate suspension, which indicates that the nitrogen remaining in the insoluble-carbon residue after digestion and washing is in what may be considered an inert form and should not be included in the humin group.

CONCLUSIONS

From the data contained in this paper the following conclusions may be drawn:

(1) The Van Slyke method for protein analysis, when applied to mixtures of casein and starch in the proportion of 1 to 5, and hydrolyzed

from 12 to 15 hours with 20 per cent hydrochloric acid gives results for the amino-acid groups that are comparable with those obtained by Van Slyke upon casein alone.

(2) A digestion period of more than 15 hours with 20 per cent hydrochloric acid on a casein-starch mixture brings about a redistribution of the nitrogen contained in the histidin and cystin groups.

(3) The insoluble residue obtained from a casein-starch digestion after being thoroughly washed contains nitrogen, which is not seriously affected when distilled with calcium-hydrate suspension, very small amounts being split off as ammonia or remaining in the filtrate. This indicates that the nitrogen is in an inert form and its estimation should not be included in the humin determination.

BEHAVIOR OF SWEET POTATOES IN THE GROUND

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THE PROBLEM

In the course of former investigations[1] on the behavior of sweet potatoes in storage, it was observed that the percentage of starch was always highest and the percentage of sugar lowest in freshly dug potatoes. This observation was more or less incidental, having been made in the course of experiments whose object was the solution of other problems. It was therefore not based upon a systematic study of the roots throughout the latter part of the growing season. Nevertheless the constancy of the condition seemed to justify the conclusion that in the growing sweet potato the reserve materials exist essentially in the form of starch, and that the appearance of sugar in considerable quantities is a phenomenon occuring only in storage or after the destruction of the leaves.

In order to determine whether these quantitative relations between the starch content and the sugar content of the sweet potato remain constant throughout the latter part of the growing season, and to what extent they are changed by the death of the vines, the carbohydrate metabolism in Big Stem sweet potatoes was followed from the time the roots were large enough to furnish the requisite samples until they were seriously damaged by frost.

The record thus obtained of the condition of the potatoes during this period may be useful as an aid in determining the time for harvesting the crop; for it is evident that, if marked changes occur in the roots during the latter part of the season, the time of harvest will depend upon the purpose for which they are destined, whether for storage, stock feed, silage, or, as Keitt has suggested, for the manufacture of starch. In the last case it is evident that the crop should be harvested when the starch content is greatest. As a rule, growers are advised to dig sweet potatoes when they are fully matured or after they have thoroughly ripened. While these phrases imply the idea that the roots reach a more or less definite state of ripeness, the characteristics by which this state may be recognized are not precisely defined. On this matter a record of the

[1] HASSELBRING, Heinrich, and HAWKINS, L. A. PHYSIOLOGICAL CHANGES IN SWEET POTATOES DURING STORAGE. *In* Jour. Agr. Research, v. 3, no. 4, p. 331–342. 1915.

—— —— CARBOHYDRATE TRANSFORMATIONS IN SWEET POTATOES. *In* Jour. Agr. Research, v. 5, no. 13, p. 543–560. 1915.

changes in the roots during the latter part of their growth may also throw some light.

PREVIOUS INVESTIGATION

The only systematic examination heretofore published on the behavior of sweet potatoes in the ground is that made in South Carolina by Keitt,[1] who investigated the behavior of four varieties during 1908 and 1909. Since his data are not easily summarized his tables recalculated on the basis of dry matter are given here for purposes of comparison with subsequent data.

TABLE I.—*Percentage composition of sweet potatoes in 1908, according to Keitt*

Date.	Variety.	Water.	Starch.	Glucose.	Sucrose.	Total carbohydrates.
Aug. 28	Nancy Hall	69.23	58.11	1.98	13.58	73.67
Sept. 7	.....do	73.34	55.93	5.93	6.83	68.69
Sept. 18	.....do	69.08	56.95	6.08	6.18	69.21
Sept. 29	.....do	68.70	63.64	7.35	4.57	75.56
Nov. 18	.....do	68.75	57.02	4.90	7.52	69.44
Aug. 28	Polo	70.76	52.94	2.77	14.16	69.87
Sept. 7	.....do	73.85	50.17	6.42	10.75	67.34
Sept. 18	.....do	77.89	51.11	8.68	9.23	69.02
Sept. 29	.....do	70.07	51.69	5.98	1.37	59.04
Nov. 18	.....do	72.53	54.06	6.37	7.35	67.78
Aug. 28	Purple yam	69.79	60.31	4.04	13.31	77.66
Sept. 7	.....do	71.65	54.14	3.67	14.04	71.85
Sept. 18	.....do	70.30	52.86	5.62	9.87	68.35
Sept. 29	.....do	71.30	63.62	7.39	5.64	76.65
Nov. 18	.....do	65.67	56.22	4.19	6.35	66.76
Aug. 28	Fulleton yam	68.40	54.08	3.70	15.98	73.76
Sept. 7	.....do	68.17	52.69	6.57	13.10	72.36
Sept. 18	.....do	67.67	54.38	10.83	6.22	71.43
Sept. 29	.....do	66.72	63.91	7.69	1.86	73.46
Nov. 18	.....do	67.74	58.03	1.61	10.42	70.06

[1] KEITT, T. E. THE FORMATION OF SUGARS AND STARCH IN THE SWEET POTATO. S. C. Agr. Exp. Sta. Bul. 136, 14 p. 1911.

——— SWEET POTATO INVESTIGATION. S. C. Agr. Exp. Sta. Bul. 165, 43 p. 1912.

TABLE II.—*Percentage composition of sweet potatoes in 1909, according to Keitt*

Date.	Variety.	Water.	Starch.	Glucose.	Sucrose.	Total carbohydrates.
Aug. 31	Pumpkin yam	72.45	58.22	13.03	2.50	73.75
Sept. 10	.....do	66.12	57.20	11.98	5.73	74.91
Sept. 21	.....do	74.27	55.03	6.18	8.94	70.15
Oct. 10	.....do	68.34	53.03	3.95	9.95	66.93
Oct. 26	.....do	70.20	59.60	4.50	14.70	78.80
Aug. 31	Purple yam	66.97	63.73	8.27	5.51	77.51
Sept. 10	.....do	64.71	61.06	9.18	3.51	73.75
Sept. 21	.....do	62.42	69.10	3.70	4.76	77.56
Oct. 2	.....do	61.59	69.72	6.77	5.18	81.67
Oct. 10	.....do	60.91	56.46	2.76	7.55	66.77
Oct. 26	.....do	63.83	71.00	4.06	6.50	81.56
Aug. 31	Polo	66.81	70.44	6.87	2.32	79.63
Sept. 10	.....do	68.24	61.52	6.99	8.88	77.39
Sept. 21	.....do	69.44	68.52	6.09	4.16	78.77
Oct. 2	.....do	67.98	64.55	4.18	3.06	71.79
Oct. 10	.....do	61.24	58.38	3.04	6.01	67.43
Oct. 26	.....do	66.08	70.70	3.33	7.61	81.64
Aug. 31	Brazilian	67.45	70.78	7.28	5.74	83.80
Sept. 10	.....do	64.31	62.96	8.21	3.98	75.15
Sept. 21	.....do	65.51	69.99	2.61	7.16	79.76
Oct. 10	.....do	66.22	55.21	3.85	7.70	66.76
Oct. 26	.....do	69.97	65.77	4.86	8.26	78.89

These figures exhibit considerable fluctuation. In 1908 there was as a rule a decrease in the percentage of starch from August 28 to September 18, then a sudden increase from September 18 to September 29, and an equally sudden fall from September 29 to November 18. A frost which killed the vines occurred on November 6. The Polo variety does not conform to the others in its behavior. During the same period all the varieties show a decrease in sucrose up to September 29, and an increase from that time until November 18. The glucose shows a gradual increase, reaching a maximum in the different varieties between September 18 and September 29, after which there is a loss of glucose. During the next year the figures show even greater irregularity. The percentage of starch fell and rose alternately between each pair of successive dates. It is notable that after the frost which killed the vines on October 13, the starch content of all varieties increased considerably. Hence, there is one year a loss of starch after the death of the vines and in the following year an increase. The figures representing the percentages of glucose and sucrose fluctuate irregularly, but in general it may be said that the glucose fell throughout the season, while the sucrose increased. It is to be noted, however, that after the frost both sugars increased. Thus, we have the remarkable phenomenon of an increase in the percentage of of total carbohydrates in the roots after the vines had been killed.

EXPERIMENTAL WORK

In the present investigation Big Stem sweet potatoes were used. They were grown at Bell Station, Maryland, in a sandy field having a gentle slope to the south. Lots of 15 to 20 kgm. were collected each week from September 18 to November 27. The collections were always made in the afternoon. The roots were thoroughly washed and stored in a covered receptacle in the laboratory until the following day, when the samples were prepared for analysis. In each case moisture, starch, cane sugar, and reducing sugar were determined in duplicate in five potatoes of the lot.

At the time of the first digging, September 18, the potatoes were still small, so that it was difficult to get roots large enough to furnish the requisite samples for analysis. After two or three weeks there was an abundance of large roots. The vines remained green and in a healthy state until the week of October 9. Heavy frosts during that week, especially on October 15, killed the leaves but not the stems. By November 7 the stems which remained green after the leaves had been killed were slowly dying, and some of the potatoes showed small round injured spots on the portions near the surface of the ground or projecting above it. On November 21 many of the roots showed considerable injury on the exposed ends, but sound potatoes were still abundant. At the time of the last collection, on November 28, the roots were so extensively damaged that it was difficult to find enough sound ones for analysis. After that date the experiment was discontinued.

The results of the analyses are given in Table III. For purposes of discussion the analytical data have been reduced to the basis of dry matter in the roots. These results are given in the left-hand part of the table. Since it may be desirable to have for reference a record of the actual percentages of the different substances contained in the potatoes, the original analytical data based on the fresh weight of the roots are given in the right-hand part of the table.

TABLE III.—*Percentage composition of Big Stem sweet potatoes in the ground during the latter part of the growing season*

Date.	Sweet potato No.	Moisture.	On the basis of dry matter.				On the basis of fresh material.		
			Starch.	Cane sugar.	Reducing sugar as glucose.	Total carbohydrates.	Starch.	Cane sugar.	Reducing sugar as glucose.
Sept. 18	1	73.38	71.37	7.36	1.20	79.93	19.00	1.96	0.32
	2	75.76	69.72	8.70	1.77	80.19	16.90	2.11	.43
	3	73.70	71.79	7.76	1.14	80.69	18.88	2.04	.30
	4	73.56	72.01	8.17	1.78	81.96	19.04	2.16	.47
	5	73.21	72.08	7.65	1.31	81.04	19.31	2.05	.35
	Average	73.92	71.39	7.93	1.44	80.76	18.63	2.06	.37
Sept. 25	6	73.34	71.53	8.63	1.31	81.47	19.07	2.30	.35
	7	72.35	72.98	7.12	.87	80.97	20.18	1.97	.24
	8	73.99	72.24	6.80	1.19	80.23	18.79	1.77	.31
	9	71.44	74.51	6.72	1.33	82.56	21.28	1.92	.38
	10	75.09	70.69	8.31	1.41	80.41	17.61	2.07	.35
	Average	73.24	72.39	7.52	1.22	81.13	19.39	2.01	.33
Oct. 2	11	74.58	69.04	8.14	1.49	78.67	17.55	2.07	.38
	12	74.76	70.44	9.27	1.62	81.33	17.78	2.34	.41
	13	73.28	71.07	9.96	1.68	82.71	18.99	2.66	.45
	14	71.07	74.59	7.71	1.45	83.75	21.58	2.23	.42
	15	75.64	69.38	8.95	2.38	80.71	16.90	2.18	.58
	Average	73.87	70.90	8.81	1.72	81.43	18.56	2.30	.45
Oct. 9	16	75.69	69.52	8.19	1.81	79.52	16.90	1.99	.44
	17	76.19	68.25	9.83	2.31	80.39	16.25	2.34	.55
	18	75.55	68.83	8.22	2.49	79.54	16.83	2.01	.61
	19	75.30	69.15	8.79	2.23	80.17	17.08	2.17	.55
	20	74.62	70.65	7.88	2.29	80.82	17.93	2.00	.58
	Average	75.47	69.28	8.58	2.23	80.09	17.00	2.10	.55
Oct. 17	21	76.34	69.82	8.37	2.49	80.68	16.52	1.98	.59
	22	76.37	69.53	8.55	3.47	81.55	16.43	2.02	.82
	23	76.57	70.00	7.68	2.99	80.67	16.40	1.80	.70
	24	76.52	68.87	8.05	2.51	79.43	16.17	1.89	.59
	25	75.68	69.00	8.92	2.59	80.51	16.78	2.17	.63
	Average	76.30	69.44	8.31	2.81	80.57	16.46	1.97	.67
Oct. 23	26	77.00	68.70	9.00	2.30	80.00	15.80	2.07	.53
	27	77.43	67.52	9.35	3.06	79.93	15.24	2.11	.69
	28	76.18	70.07	8.61	2.06	80.74	16.69	2.05	.49
	29	78.87	67.87	8.00	3.69	79.56	14.34	1.69	.78
	30	77.66	68.40	9.36	2.91	80.67	15.28	2.09	.65
	Average	77.43	68.51	8.86	2.80	80.18	15.47	2.00	.63

TABLE III.—*Percentage composition of Big Stem sweet potatoes in the ground during the latter part of the growing season*—Continued

Date.	Sweet potato No.	Moisture.	On the basis of dry matter.				On the basis of fresh material.		
			Starch.	Cane sugar.	Reducing sugar as glucose.	Total carbohydrates.	Starch.	Cane sugar.	Reducing sugar as glucose.
Oct. 30	31	77.00	65.52	10.65	2.87	79.04	15.07	2.45	0.66
	32	77.91	65.05	11.77	2.81	79.63	14.37	2.60	.62
	33	77.66	65.22	10.56	2.91	78.69	14.57	2.36	.65
	34	78.79	59.74	14.47	4.24	78.45	12.67	3.07	.90
	35	77.52	67.70	8.76	2.98	79.44	15.22	1.97	.67
	Average	77.78	64.65	11.24	3.16	79.05	14.38	2.49	.70
Nov. 6	36	76.17	62.82	14.65	3.40	80.87	14.97	3.49	.81
	37	76.11	64.92	14.15	2.68	81.75	15.51	3.38	.64
	38	76.59	61.90	14.44	2.95	79.29	14.49	3.38	.69
	39	74.71	65.01	11.82	1.86	78.69	16.44	2.99	.47
	40	76.37	63.27	13.67	2.58	79.52	14.95	3.23	.61
	Average	75.99	63.58	13.75	2.69	80.02	15.27	3.29	.64
Nov. 13	41	78.02	59.55	15.24	2.59	77.38	13.09	3.35	.57
	42	78.23	54.89	18.56	2.99	76.44	11.95	4.04	.65
	43	77.14	57.13	18.20	2.45	77.78	13.06	4.16	.56
	44	78.83	51.54	20.08	3.40	75.02	10.91	4.25	.72
	45	78.32	53.23	19.93	5.03	78.19	11.54	4.32	1.09
	Average	78.14	55.27	18.40	3.29	76.96	12.11	4.02	.72
Nov. 20	46	76.99	52.41	20.99	3.30	76.70	12.06	4.83	.76
	47	79.22	48.32	25.31	3.75	77.38	10.04	5.26	.78
	48	76.02	55.46	19.72	2.79	77.97	13.30	4.73	.67
	49	79.45	46.76	25.16	3.41	75.33	9.61	5.17	.70
	50	77.20	50.70	24.39	2.76	77.85	11.56	5.56	.63
	Average	77.78	50.73	23.11	3.20	77.03	11.31	5.11	.71
Nov. 27	51	79.93	43.70	28.10	5.08	76.88	8.77	5.64	1.02
	52	78.64	47.85	26.59	3.60	78.04	10.22	5.68	.77
	53	79.71	44.36	26.61	4.04	75.01	9.00	5.40	.82
	54	78.37	47.06	25.52	3.61	76.19	10.18	5.52	.78
	55	77.98	48.05	23.48	2.91	74.44	10.58	5.17	.64
	Average	78.93	46.20	26.06	3.85	76.11	9.75	5.48	.81

An examination of Table III shows that the sweet potatoes exhibit some individual fluctuation in composition, but these variations are not sufficiently great to obscure the seasonal trend. They show, however, that small deviations in the general contour of the seasonal changes are to be expected where so small a number of individuals is examined. The significant changes lie clearly outside the limits of the individual fluctuations. The seasonal changes in the percentage of the various constituents of the sweet potato as shown by the table are briefly described below.

MOISTURE.—The moisture content of the roots remained almost uniform during the period covered by the first three collections, from September 18 to October 2. After that time there was a gradual increase in the percentage of moisture until the end of the season. A small fluctuation appears in the lot collected on November 6. The changes in water content of the roots are therefore fairly regular and uniform. No such marked fluctuations as those recorded in the tables of Keitt are evident from these data. The beginning of the accumulation of moisture in the roots is practically coincident with the destruction of the leaves.

STARCH.—The percentage of starch in the dry matter of the roots shows a slight decrease from September 18 until October 23, varying during that period between 71.39 per cent and 68.51 per cent. On October 30, the date of the next collection, the starch content had fallen to 64.65 per cent. From that date the starch content continued to fall until the end of the season, when the minimum of 46.20 per cent was reached. The rapid disappearance of starch follows, somewhat delayed, upon the death of the leaves.

CANE SUGAR.—The cane-sugar content remains practically constant between 7.52 and 8.86 per cent until the time when the percentage of starch begins to fall rapidly. With the decrease in starch the cane sugar begins to increase correspondingly until it finally represents 26.06 per cent of the dry matter of the roots. It should be noted, however, that in general the changes in cane sugar are inaugurated somewhat later than those of the starch.

REDUCING SUGAR.—The reducing sugar content remains constant at first and then shows a gradual rise until the final percentage is somewhat more than double that at the beginning. The increase in reducing sugar antecedes somewhat the rise in cane sugar. It is noteworthy also that under these conditions reducing sugar apparently does not accumulate to the same extent to which it accumulates in sweet potatoes in storage.

TOTAL CARBOHYDRATES.—The total carbohydrate content undergoes very little change until toward the end of the season, when the roots begin to show marked injury by frost. At that time an evident loss of carbohydrates becomes apparent. The constancy of the total carbohydrate content of the sweet potato is in marked contrast to the fluctuations observed by Keitt.

The foregoing facts have been embodied in the curves in figure 1. The curves are based on the averages of the analyses for each week.

CONCLUSIONS

It may be concluded from this investigation that the changes occurring in sweet potatoes in the ground during the later part of the growing season proceed in a regular and orderly manner. During the later part of the period of growth the composition of the roots remains remarkably uniform, and presents no striking or irregular fluctuations. During this

period the root is characterized by a high starch content, and a low sugar content. The changes which occur later are associated with the death of the vines. Prominent among these changes is the accumulation of water in the roots as a result of the cessation of transpiration in conse-

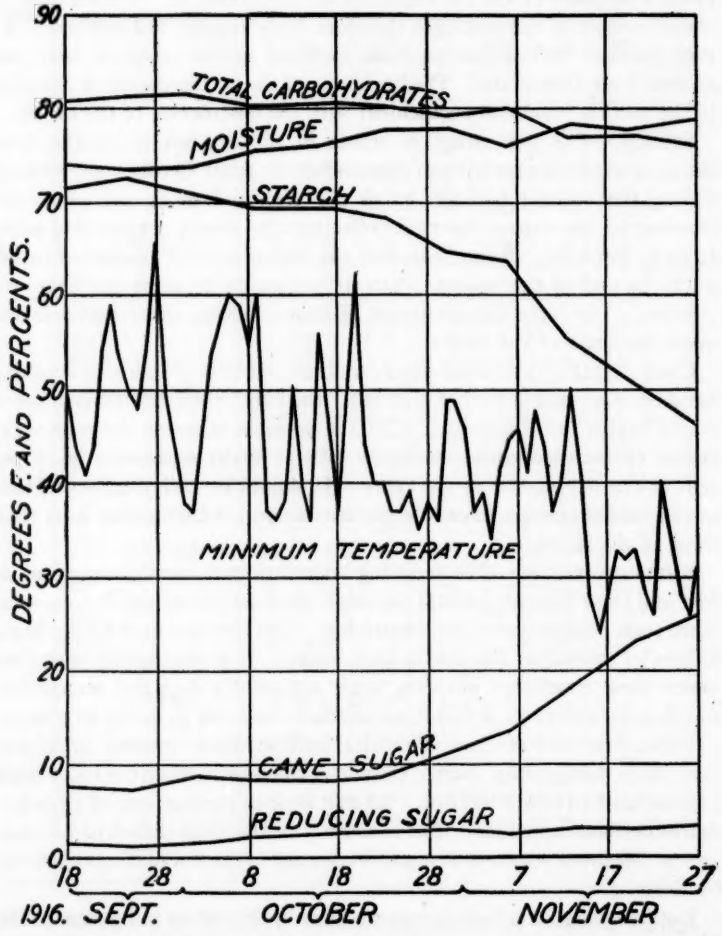

FIG. 1.—Graphs showing changes in composition of Big Stem sweet potatoes during the latter part of the season, from September 18 to November 27, and the minimum temperatures at the United States Weather Bureau Observatory at Washington, D. C., some 20 miles distant, during that period. The ordinates indicate percentages in the one case and degrees Fahrenheit in the other.

quence of the destruction of the leaves. With the termination of the flow of materials from the vines the carbohydrate transformations characteristic of sweet potatoes in storage are inaugurated. These changes consist in the transformation of starch into sugars. In point

of time the decrease in starch and the increase in reducing sugar precede somewhat the increase in cane sugar. It appears, therefore, that reducing sugar is formed first as an intermediate step in the change from starch to cane sugar. The loss caused by respiration, which is considerable during the curing process and in storage, is apparently slight in sweet potatoes in the ground. Appreciable destruction of carbohydrates appears not to occur under these conditions until late in the season when the roots have been injured by frosts.

The changes here described have a practical bearing on the question of maturation of sweet potatoes and on the choice of the time of harvest. Since the carbohydrate relations of the roots in the ground remain practically unchanged while the vines are uninjured, the roots can not be said to undergo a definite process of ripening, in the sense of a progressive transformation of one reserve substance into another, such as the change of insoluble pectin into soluble pectin derivatives in the peach, or the transformation of starch into cane sugar and invert sugar in the apple. Under ordinary conditions the potatoes continue to grow until frost without reaching any definite state of maturity recognizable by progressive changes in the reserve materials which they contain. The changes in storage, which may perhaps be regarded as a process of maturation, do not come in for consideration here, since statements relating to the degree of maturity of sweet potatoes always refer to the growing roots. It is evident from these considerations that the choice of time of harvest is not a matter of maturity of the roots, but is governed by other factors. The potatoes may safely be kept in the ground until the leaves have been injured by frost.

Of the changes which occur after the destruction of the leaves, the accumulation of water in the roots deserves foremost consideration. It can scarcely be doubted that this increased water content is detrimental to the successful storage of the roots, and causes them to be more subject to decay than roots of normal water content. One of the objects of the rather expensive operation of curing is to eliminate a part of the water contained in the roots. As a rule observers agree that cured sweet potatoes keep better than uncured ones. Only occasionally a statement to the contrary is found. It may therefore safely be assumed that the increase in the relative proportion of water in the roots will be detrimental to storage. On this account it is of utmost importance that the harvesting of sweet potatoes be not long delayed after the leaves have been killed by frost. The other changes occurring in sweet potatoes in the ground are essentially the same as the changes occurring in storage. These changes are therefore in no way detrimental to the crop, since no appreciable loss of carbohydrates occurs until the roots have been so severely injured that they have lost their market value.

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STUDIES IN SOIL REACTION AS INDICATED BY THE HYDROGEN ELECTRODE

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INTRODUCTION

There has been developed in the past few years a rather voluminous literature dealing with the subject of soil reaction. One has only to scan this literature in order to find wide variations of opinion between investigators as to the cause and nature of soil acidity.

Until recently the various qualitative and quantitative methods in vogue for indicating soil acidity or lime requirement have not been sufficiently delicate to draw definite conclusions as to the "true reaction" of soils. The lack of uniformity and accuracy of methods has undoubtedly caused such confusion on this subject. By adopting modern methods for measuring soil reaction many of the contentions should be obliterated.

Though the hydrogen electrode has been used for some time in indicating changes in reaction, Gillespie (*7*) [1] was the first to use it on an extended scale as an indicator of reaction in soils. Sharp and Hoagland (*12*) have since measured the H-ion concentration of a number of oils in suspension, and have extended this method to studying other soil phenomena.

The significance of the terms "true acidity," "true alkalinity," and "true neutrality" need not be defined here, except in so far as an explanation of the method adopted in reporting results obtained. Pure water dissociates into H and OH ions in equal concentration. The product of the concentration of these ions in a solution is a constant, approximately $1 \times 10-14$. When the H ions are present in a concentration greater than $1 \times 10-7$, the solution is acid; the presence of OH ions in greater concentrations than $1 \times 10-7$ results in an alkaline solution. For a more detailed discussion of this subject, the reader is referred to texts on electrochemistry.

The investigations herein reported were begun about the time of the appearance of Sharp and Hoagland's paper, to ascertain if appreciable differences occurred in the H-ion concentration of soils of humid regions, especially from those of the Southern States. It would appear that with the excessive rainfall of this region an accumulation of soluble acids in the soil would be almost impossible.

[1] Reference is made by number (italic) to "Literature cited," p. 30-31.

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The method has been used for indicating the reaction of the soil film water. The effects of several fertilizer materials have been studied on the H-ion concentration of various field soils, receiving applications of such fertilizers for a number of years. Lastly, the effect of ammonium sulphate and monocalcium phosphate on the reaction of soil film water have been investigated.

METHODS OF INVESTIGATION

The apparatus for measuring the H-ion concentration of soil suspensions and extracts was essentially that described by Hildebrand (*8*), and modified by Sharp and Hoagland. Palladium was substituted for platinum as the electrode, which was treated in a manner similar to that described by Findlay (*6*) for coating electrodes. The supply of hydrogen was obtained by electrolyzing water, with potassium hydroxid as the electrolyte. All the precautions of rigidity of connections, insulation of apparatus, time (which often varied) for establishment of equilibrium between soil and solution, coating electrodes, and prevention of loss of CO_2 were strictly observed.

It might be said in passing that no difficulties were encountered due to the reduction of nitrates to ammonia, as has been suggested.

In the preparation of soil suspensions, unless otherwise stated, the arbitrary ratio of 10 gm. of air-dried soil to 100 c. c. of as pure distilled water as obtainable was used. In the case of field soils their content was determined as soon after sampling as practicable, and the same ratio of soil to water maintained. All samples except those taken directly from the field were screened through a 2-mm. sieve.

In all cases the readings became constant in a few minutes. Duplicate readings on the same sample of soil could easily be read to 0.02 volt. However, to be certain that equilibrium had been established the electrode was allowed to remain in contact with solution for 30 minutes. It was almost impossible to get such closely agreeing results as 0.02 volt with different samples of the same soil. This can be accounted for in the lack of uniformity of mixing.

The results are reported in the usual manner for such measurements, units of gram-molecules of H ion per liter. The tables of Schmidt (*11*) were used in securing the H-ion concentration from the voltmeter readings.

RESULTS OBTAINED

In Table I will be found the results of measurements of the H-ion concentrations of 68 samples of untreated soils, including subsoils, which represent a wide range in types of five series. Included in this table are results derived from five samples of treated soil. The samples are taken as a fair representation of the soils common to the area of the southeastern portion of the United States, which extends from and including the Appalachian Mountains to the Atlantic Ocean.

TABLE I.—*Hydrogen-ion concentration of soil suspensions*

Sample No.	Soil type.[a]	Depth.	Voltmeter readings.	H-ion concentration.
		Inches.		*Gram molecules per liter.*
1565	Norfolk sand (sand-hill phase)	0–4	0.700	0.4×10^{-6}
1566	.....do	4–21	.684	$.9\times10^{-6}$
1067	.....do	0–4	.712	$.3\times10^{-6}$
1068	.....do	4–18	.706	$.3\times10^{-6}$
1501	Norfolk coarse sandy loam	0–6	.684	$.9\times10^{-6}$
1502	.....do	6–28	.684	$.9\times10^{-6}$
1287	.....do	0.6	.696	$.5\times10^{-6}$
1288	.....do	6–26	.681	1.0×10^{-6}
1397	Norfolk sandy loam	0–7	.674	$.1\times10^{-5}$
1398	.....do	7–28	.668	$.1\times10^{-5}$
1483	.....do	0–7	.662	$.2\times10^{-5}$
1484	.....do	7–28	.674	$.1\times10^{-5}$
1344	Norfolk fine sandy loam	0–6	.660	$.2\times10^{-5}$
1345	.....do	6–36	.671	$.1\times10^{-5}$
991	.....do	0–6	.645	$.4\times10^{-5}$
992	.....do	6–36	.640	$.5\times10^{-5}$
1551	Norfolk very fine sandy loam	0–6	.657	$.2\times10^{-5}$
1552	.....do	6–24	.660	$.2\times10^{-5}$
1029	.....do	0–8	.614	$.1\times10^{-4}$
1030	.....do	8–30	.583	$.5\times10^{-4}$
1519	Norfolk silt loam	0–6	.574	$.7\times10^{-4}$
1520	.....do	6–28	.568	$.9\times10^{-4}$
1499	.....do	0–6	.560	$.1\times10^{-3}$
1500	.....do	6–32	.555	$.1\times10^{-3}$
1352	Cecil coarse sandy loam	0–7	.712	$.3\times10^{-5}$
1353	.....do	7–20	.699	$.5\times10^{-5}$
1287	.....do	0–6	.706	$.3\times10^{-5}$
1288	.....do	6–30	.700	$.4\times10^{-5}$
1125	Cecil fine sandy loam	0–8	.702	$.4\times10^{-5}$
1126	.....do	8–24	.681	1.0×10^{-5}
1261	.....do	0–8	.699	$.4\times10^{-5}$
1262	.....do	8–26	.673	$.1\times10^{-5}$
1336	Cecil clay loam	0–6	.652	$.3\times10^{-5}$
1337	.....do	6–30	.666	$.1\times10^{-5}$
1205	.....do	0–6	.659	$.2\times10^{-5}$
1333	.....do	6–36	.643	$.5\times10^{-5}$
1322	Cecil clay	0–7	.641	$.5\times10^{-5}$
1323	.....do	7–20	.582	$.5\times10^{-4}$
1435	.....do	0–6	.646	$.4\times10^{-5}$
1436	.....do	6–36	.607	$.1\times10^{-4}$
1121	Iredell fine sandy loam	0–6	.732	$.1\times10^{-5}$
1122	.....do	6–36	.738	$.1\times10^{-5}$
1344	.....do	0–8	.711	$.3\times10^{-5}$
1345	.....do	8–24	.704	$.4\times10^{-5}$
1328	Iredell loam	0–8	.692	$.6\times10^{-5}$
1329	.....do	8–24	.714	$.2\times10^{-5}$
1257	.....do	0–6	.684	$.9\times10^{-6}$
1258	.....do	6–26	.679	$.1\times10^{-5}$
395	Porter's sand	0–6	.673	$.1\times10^{-5}$
396	.....do	6–20	.668	$.1\times10^{-5}$
397	.....do	0–6	.640	$.5\times10^{-5}$
398	.....do	6–20	.638	$.5\times10^{-5}$
639	Porter's sandy loam	0–7	.648	$.3\times10^{-5}$
640	.....do	7–28	.641	$.5\times10^{-5}$
6652	.....do	0–7	.656	$.2\times10^{-5}$
653	.....do	7–30	.649	$.3\times10^{-5}$
1201	Porter's loam	0–8	.644	$.4\times10^{-5}$

[a] The writer is indebted to Dr. W. H. McIntire, of the Tennessee Agricultural Experiment Station, for the samples of the treated soils.

TABLE I.—*Hydrogen-ion concentration of soil suspensions*—Continued

Sample No.	Soil type.	Depth.	Voltmeter readings.	H-ion concentration.
		Inches.		*Gram molecules per liter.*
1202	Porter's loam	8–30	.639	$.5\times10^{-5}$
1372	.....do	0–7	.647	$.3\times10^{-5}$
1373	.....do	7–24	.639	$.5\times10^{-5}$
674	Porter's clay	0–7	.577	$.6\times10^{-4}$
675	.....do	7–24	.566	$.1\times10^{-3}$
684	.....do	0–6	.594	$.3\times10^{-4}$
685	.....do	6–20	.587	$.4\times10^{-4}$
1007	Muck	0–18	.483	$.2\times10^{-2}$
1212	.....do	0–24	.462	$.6\times10^{-2}$
1077	.....do	0–36	.536	$.3\times10^{-3}$
2526	.....do	0–36	.427	$.2\times10^{-1}$
	Chickamauga limestone soil[a]	.....	.864	$.7\times10^{-9}$
	Chickamauga limestone soil[b]	.....	.824	$.3\times10^{-8}$
	Cumberland loam[a]	.....	.893	$.2\times10^{-9}$
	Cumberland loam[b]	.....	.856	$.9\times10^{-9}$
	Tillico sandy loam[a]	.....	.866	$.6\times10^{-9}$

[a] Treated in 1912 with 16,000 pounds of calcium carbonate per acre in excess of Vietch indication.
[b] Treated in 1912 with $MgCO_3 \rightleftharpoons CaCO_3$ at rate of 16,000 pounds per acre in excess of Vietch indication.

The results shown in Table I indicate wide variations in the H-ion concentrations of the untreated soils under experiment. This varies from very nearly neutral in some of those of the Iredell series to rather excessive acidity in the Norfolk silt loam and mucks. This is in accord with what would be expected. The Iredell soils are of residual origin formed from basic eruptions, mainly diorite. The amount of basic elements supplied this soil is greatly in excess of those commonly found in the area included in this study. The Norfolk silt loam being a transported soil, was formed under conditions through which the basic elements have been removed. It also contains rather high amounts of partially decomposed organic matter, and should show a high concentration of H over OH ions. Field and pot tests with various crops have shown indications of excessive acidity on some of the muck soils. Indeed on some of the muck fields from which the samples were taken little or none of the common agricultural crops will thrive until the land has been limed.

No definite relationship appears to exist between the H-ion concentration and types of different texture. It can be noticed that there is a tendency for the H ion to increase as the number of fine particles increase in a series. However, there are exceptions. The clay loams and loams of the Iredell and Porter's series show greater H-ion concentration than do those of coarser texture. It may be observed that in many cases the subsoil shows a greater degree of acidity than the corresponding surface soil. The general practice in farming these soils has been the removal from the land of all crops. Probably there is a tendency for plant roots to remove more bases from lower depths than from the surface.

The samples of soil which have been treated with excessive amounts of calcium and magnesium carbonate show a greater concentration of OH than H ions in solution. Dr. McIntire informed the writer that the carbonates have long since disappeared in these soils. Obviously the new compounds of calcium and magnesium, whatever they may be, give a strong basic reaction.

These results bear out very forcibly the contentions of Gillespie (7) and Sharp and Hoagland (*12*) that there is a preponderance of H over OH ions in the liquid phase of many soil suspensions. Whether the "true acidity" as indicated from the results of Table I is developed from organic acids or acid silicates can not be stated. In some of the sandy soils the organic matter is quite low, yet indications lead to the conclusion that there is a greater concentration of H ions than found in neutral solutions. With the muck samples the organic-matter content is very high, being 90 per cent or more, and most marked acidity is shown.

H-ION CONCENTRATION OF SOIL FILM OR CAPILLARY WATER

The question has often been raised, "Is the water held as a liquid film around the soil particles of different reaction from that in the free state?" The difficulty encountered in securing any workable amount of the film water has militated against any direct study of this question. Recently, Morgan (*9*) has devised a workable modification of the "oil displacement" method for obtaining the soil solution in an unaltered form. A study of this water should throw much light on some of the obscure problems of soils. One serious difficulty yet remains with the method, which is its inability to get back all of water held as thin films around the soil grains. However, a study of the reaction of that portion of the film water obtainable should give indications of value as to the conditions of the soil solution.

The Morgan apparatus, with a few unimportant modifications, has been used in obtaining that portion of the capillary water displaced by paraffin oil under high pressure. The oil used in this work was the purest obtainable. As far as could be noticed, it gave a neutral reaction with the hydrogen-electrode apparatus and by titrating against standard alkali with methyl orange, methyl red, and phenolpthalein as indicators.

Some of the soil samples used were taken directly from the filed; others had been stored in the laboratory for a number of years. The portion which passed a 2-mm. sieve was thoroughly mixed, and the water content determined. Sufficient distilled water was added to bring the moisture content up to about what is considered the optimum for that soil. Water lost through evaporation was replaced at frequent intervals, after which the soils were thoroughly packed in the cylinder and treated with oil under high pressure.

The results of this investigation are shown in Table II

TABLE II.—*Reaction of soil-film water*

Soil type.	Film water.					Free water.			Voltmeter readings.	H-ion concentration.
	Amount of soil.	Moisture content (per liter dry basis).	Moisture recovered.	Time of contact.	Volume of film water.	Amount of soil.	Amount of water.	Time of contact.		
	Lbs.	*P. ct.*	*P. ct.*	*Days.*	*C. c*	*Gm.*	*C. c.*	*Days.*		*Gram-molecules per liter.*
Cecil clay loam	10	25	7.2	4	50	.....	.....	.....	0.572	$0.8+10^{-4}$
Do	10	25	6.9	4	50	.....	.....	.....	.588	$.4+10^{-4}$
Do	.....	.....	.....	.....	.....	5	50	4	.679	$.1+10^{-5}$
Porter's loam	10	25	6.4	4	50	.....	.....	.....	.593	$.3+10^{-4}$
Do	10	25	4.9	4	50	.....	.....	.....	.604	$.2+10^{-4}$
Do	.....	.....	.....	.....	.....	5	50	4	.684	$.9+10^{-6}$
Norfolk fine sandy loam	10	20	15.3	3	50	.....	.....	.....	.614	$.1+10^{-4}$
Do	10	20	13.3	3	50	.....	.....	.....	.624	$.1+10^{-4}$
Do	.....	.....	.....	.....	.....	5	50	3	.661	$.2+10^{-5}$
Norfolk sand	10	15	18.4	2	50	.....	.....	.....	.666	$.1+10^{-5}$
Do	10	15	20.6	2	50	.....	.....	.....	.654	$.3+10^{-5}$
Do	.....	.....	.....	.....	.....	5	50	2	.694	$.6+10^{-6}$
Tellico sandy loam [a]	5	20	12.8	3	25	.....	.....	.....	.929	$.5+10^{-10}$
Do	.....	.....	.....	.....	.....	2.5	25	3	.877	$.4+10^{-9}$
Chickamauga limestone soil [a]	5	25	7.7	3	25	.....	.....	.....	.976	$.8+10^{-11}$
Do	.....	.....	.....	.....	.....	2.5	25	3	.896	$.1+10^{-9}$

[a] Sufficient soil not available for duplicate extractions.

The data presented in Table II show rather conclusively that the soil-film water has the same reaction as the free water. The difference is only in degree of intensity. Those soils which showed an acid reaction in suspensions gave a greater concentration of H ions in the film water. Conversely, those which indicated a greater OH-ion concentration than H in suspension gave a greater intensity of OH ions in the solution. These results are not in keeping with those of Sharp and Hoagland (*12*), who found no appreciable change in H or OH ions in varying the proportions of soil to water in making suspensions.

With the freezing-point method for measuring the concentration of the soil solution Bouyoucos and McCool (*3*) show that as the amount of water decreases in an arithmetic progression the lowering of the freezing point (increase in concentration) increases in a geometric progression. This apparently is due to the rendering inactive of a portion of the water in the soils, hence this water does not take part in dissolving the solutes of the soil. That portion left free or uncombined becomes highly charged with soluble salts and gives phenomenal increases in the freezing-point lowering. The same line of reasoning may be applied to the increase in intensity of reaction of film water when compared to that of soil suspensions.

With the heavier types of soil only a small percentage of the added water was recovered. It would be of extreme interest to note the intensity of reaction of the thinnest moisture film which could remain in contact with the soil grains. In other words, all of the liquid added to the soil should be recovered and studied.

EFFECT OF FERTILIZER MATERIALS ON SOIL REACTION

It has frequently been stated that certain fertilizer materials, more especially ammonium sulphate and acid phosphate, increase the acidity of soils. To obtain additional evidence, the H-ion concentration of soil suspensions have been measured in samples taken from the fertilizer plots of the North Carolina Experiment Station. Some of the soils have received annual applications of these fertilizers for as many as 15 years. All fields are located on well-defined soil types for each area of the State. Three distinct types have been studied.

The samples of both soil and subsoil were collected as carefully as possible. Borings were made at several points on the plots for both surface and subsoil samples. These were taken to the laboratory as quickly as possible and thoroughly mixed, after which water was determined in each composite sample. The ratio of water to soil was kept the same as with the air-dried soils.

Table III gives a compilation of the total amount of each fertilizer material and lime which has been applied to the plots at the different branch stations.

TABLE III.—*Total quantity (in pounds per acre) of fertilizer materials applied to experimental plots*

Branch station.	Ammonium sulphate (20 per cent nitrogen).	Sodium nitrate (14 per cent nitrogen).	Dried blood (14 per cent nitrogen).	Acid phosphate (16 per cent phosphorus pentoxid).	Potassium sulphate, (40 per cent potassium oxid).	Lime (90 per cent calcium carbonate).
Buncombe	.....	.....	4,826	1,846	1,100	6,000
Iredell	577	675	1,288	3,332	540	4,000
Central	577	675	.....	3,237	307	4,000
Edgecombe	577	675	1,638	3,372	457	4,000

The data secured from the measurements of the H-ion concentration of plots fertilized with ammonium sulphate and sodium nitrate are given in Table IV.

Marked increases in acidity can be noticed in samples taken from plots fertilized with ammonium sulphate. In every case pronounced increase of H ions is evident, and extends to the subsoil in all of the fields studied. On the Norfolk fine sandy loam more acidity is noted in the subsoil than surface.

There does not appear to be any relationship between texture and development of acidity by ammonium sulphate. This is in agreement with the work of Allison and Cook (*1*).

The results secured from the sodium-nitrate plots are in harmony with the accepted theory regarding its effect on soil reaction. A reduction of acidity is apparent.

TABLE IV.—*Effect of ammonium sulphate and nitrate of soda on the H-ion concentration of field-soil suspensions*

Branch station.	Year of beginning experiment.	Soil type.	Depth.	Treatment.	Voltmeter readings.	H-ion concentration.
			Inches.			*Gram-molecules per liter.*
Iredell	1907	Cecil clay loam	0–6	Ammonium sulphate	0.542	0.2×10^{-5}
Do	1907	do	6–24	do	.568	$.9\times10^{-4}$
Do	1907	do	0–6	Sodium nitrate	.694	$.6\times10^{-6}$
Do	1907	do	6–24	do	.678	$.1\times10^{-6}$
Do	1907	do	0–6	Untreated	.656	$.2\times10^{-6}$
Do	1907	do	6–24	do	.649	$.3\times10^{-6}$
Central	1907	Durham sandy loam	0–8	Ammonium sulphate	.548	$.2\times10^{-6}$
Do	1907	do	8–24	do	.582	$.5\times10^{-4}$
Do	1907	do	0–8	Sodium nitrate	.671	$.1\times10^{-6}$
Do	1907	do	8–24	do	.656	$.2\times10^{-6}$
Do	1907	do	0–8	Untreated	.613	$.1\times10^{-4}$
Do	1907	do	8–24	do	.603	$.2\times10^{-4}$
Edgecombe	1907	Norfolk fine sandy loam	0–6	Ammonium sulphate	.556	$.1\times10^{-5}$
Do	1907	do	6–24	do	.548	$.2\times10^{-5}$
Do	1907	do	0–6	Sodium nitrate	.666	$.1\times10^{-6}$
Do	1907	do	6–24	do	.648	$.3\times10^{-6}$
Do	1907	do	0–6	Untreated	.646	$.4\times10^{-6}$
Do	1907	do	6–24	do	.628	$.8\times10^{-6}$

EFFECT OF POTASSIUM SULPHATE ON SOIL REACTION

Skinner and Beattie (*13*) and others have observed that potassium sulphate increased the lime requirement of soils. Measurements have been made of the H-ion concentration of soil suspensions from plots to which have been added different amounts of this salt. These data are given in Table V.

TABLE V.—*Effect of potassium sulphate on the H-ion concentration of field-soil suspensions*

Branch station.	Year of beginning experiment.	Soil type.	Depth.	Treatment.	Voltmeter readings.	H-ion concentration.
			Inches.			*Gram-molecules per liter.*
Buncombe	1911	Porter's loam	0–8	Dried blood	0.656	0.2×10^{-5}
Do	1911	do	8–24	do	.654	$.3\times10^{-5}$
Do	1911	do	0–8	Dried blood, potassium sulphate.	.623	$.1\times10^{-4}$
Do	1911	do	8–24	do	.623	$.1\times10^{-4}$
Do	1911	do	0–8	Potassium sulphate	.609	$.1\times10^{-4}$
Do	1911	do	8–24	do	.596	$.3\times10^{-4}$
Do	1911	do	0–8	Untreated	.648	$.3\times10^{-5}$
Do	1911	do	8–24	do	.651	$.3\times10^{-5}$
Iredell	1903	Cecil clay loam	0–8	Dried blood	.682	$.1\times10^{-5}$
Do	1903	do	8–36	do	.671	$.1\times10^{-5}$
Do	1903	do	0–8	Dried blood, potassium sulphate.	.630	$.8\times10^{-5}$
Do	1903	do	8–36	do	.618	$.1\times10^{-4}$
Do	1903	do	0–8	Potassium sulphate	.621	$.1\times10^{-4}$
Do	1903	do	8–36	do	.608	$.1\times10^{-4}$
Do	1903	do	0–8	Untreated	.676	$.1\times10^{-5}$
Do	1903	do	0–36	do	.672	$.1\times10^{-5}$
Edgecombe	1903	Norfolk fine sandy loam	0–8	Dried blood	.632	$.7\times10^{-5}$
Do	1903	do	8–24	do	.620	$.1\times10^{-4}$
Do	1903	do	0–8	Dried blood, potassium sulphate.	.602	$.2\times10^{-4}$
Do	1903	do	8–24	do	.590	$.3\times10^{-4}$
Do	1903	do	0–8	Potassium sulphate	.596	$.3\times10^{-4}$
Do	1903	do	8–24	do	.600	$.2\times10^{-4}$
Do	1903	do	0–8	Untreated	.634	$.6\times10^{-5}$
Do	1903	do	8–24	do	.628	$.8\times10^{-5}$

Slight increase in the H-ion concentration was obtained from the plots to which potassium sulphate had been applied. However, nothing like as marked an effect in producing "true acidity" is found on these plots as those to which have been added ammonium sulphate. Why this should be is not clear, unless it has been caused by nitric acid developed by the soil organisms.

EFFECT OF ACID PHOSPHATE AND LIME ON SOIL REACTION

Table VI gives the results from the plots which have received annual applications of acid phosphate and lime.

TABLE VI.—*Effect of acid phosphate and lime on the H-ion concentration of field-soil suspensions*

Branch station.	Year of beginning experiment.	Soil type.	Depth.	Treatment.	Voltmeter readings.	H-ion concentration.
			Inches.			*Gram-molecules per liter.*
Buncombe	1911	Porter's loam	0–8	Dried blood	0.656	0.2×10^{-5}
Do	1911	do	8–30	do	.654	$.3\times10^{-5}$
Do	1911	do	0–8	Acid phosphate	.662	$.2\times10^{-5}$
Do	1911	do	8–30	do	.655	$.2\times10^{-5}$
Do	1911	do	0–8	Dried blood, acid phosphate.	.652	$.3\times10^{-5}$
Do	1911	do	8–30	do	.660	$.2\times10^{-5}$
Do	1911	do	0–8	Dried blood, acid phosphate, potassium sulphate.	.612	$.1\times10^{-4}$
Do	1911	do	8–30	do	.610	$.1\times10^{-5}$
Do	1911	do	0–8	Dried blood, acid phosphate, potassium sulphate, lime.	.702	$.4\times10^{-6}$
Do	1911	do	8–30	do	.716	$.2\times10^{-6}$
Do	1911	do	0–8	Lime	.728	$.1\times10^{-6}$
Do	1911	do	8–30	do	.736	$.1\times10^{-6}$
Do	1911	do	0–8	Untreated	.648	$.3\times10^{-5}$
Do	1911	do	8–30	do	.651	$.3\times10^{-5}$
Iredell	1903	Cecil clay loam	0–6	Dried blood	.682	1.0×10^{-6}
Do	1903	do	6–30	do	.671	$.1\times10^{-5}$
Do	1903	do	0–6	Acid phosphate	.674	$.1\times10^{-5}$
Do	1903	do	6–30	do	.679	$.1\times10^{-5}$
Do	1903	do	0–6	Dried blood, acid phosphate.	.684	$.9\times10^{-6}$
Do	1903	do	6–30	do	.666	$.1\times10^{-5}$
Do	1903	do	0–6	Dried blood, acid phosphate, potassium sulphate.	.613	$.1\times10^{-4}$
Do	1903	do	6–30	do	.609	$.1\times10^{-4}$
Do	1903	do	0–6	Dried blood, acid phosphate, potassium sulphate, lime.	.712	$.3\times10^{-6}$
Do	1903	do	6–30	do	.732	$.1\times10^{-6}$
Do	1903	do	0–6	Lime	.746	$.7\times10^{-7}$
Do	1903	do	6–30	do	.754	$.5\times10^{-7}$
Do	1903	do	0–6	Untreated	.666	$.1\times10^{-5}$
Do	1903	do	6–30	do	.651	$.3\times10^{-5}$
Edgecombe	1903	Norfolk fine sandy loam	0–6	Dried blood	.632	$.7\times10^{-5}$
Do	1903	do	6–24	do	.620	$.1\times10^{-4}$
Do	1903	do	0–6	Acid phosphate	.624	$.1\times10^{-4}$
Do	1903	do	6–24	do	.624	$.1\times10^{-4}$
Do	1903	do	0–6	Dried blood, acid phosphate.	.614	$.1\times10^{-4}$
Do	1903	do	6–24	do	.609	$.1\times10^{-4}$
Do	1903	do	0–6	Dried blood, acid phosphate, potassium sulphate.	.600	$.2\times10^{-4}$
Do	1903	do	6–24	do	.592	$.3\times10^{-4}$
Do	1903	do	0–6	Dried blood, acid phosphate, potassium sulphate, lime.	.712	$.3\times10^{-6}$
Do	1903	do	6–24	do	.716	$.2\times10^{-6}$
Do	1903	do	0–6	Lime	.726	$.1\times10^{-6}$
Do	1903	do	6–24	do	.744	$.8\times10^{-7}$
Do	1903	do	0–6	Untreated	.638	$.5\times10^{-5}$
Do	1903	do	6–24	do	.628	$.8\times10^{-5}$

The results from the plots to which acid phosphate has been added do not show any greater H-ion concentration than the ones used as controls. These plots have received rather heavy annual applications of this fertilizer for the past 15 years, the total amount applied being over 3,000 pounds per acre. The fine sandy loam may be some exception. In this case the readings are so nearly the same as from those plots which have received no fertilizer that the differences are within the range of experimental error. Indeed there is as much evidence in indicating an increased basicity from the use of acid phosphate in the clay loam and loam as from an increase in acidity in the sandy loam. This is in agreement with the more recent work of Conner (*5*), Brooks (*4*), and Bear and Salter (*2*).

Additions of lime alone or lime in combinations with the fertilizer materials have materially reduced the acidity in all plots. This is often more marked in the subsoil than in the surface. With the exception of the Cecil clay loam, lime has not been used in sufficient amounts to produce basicity.

EFFECT OF AMMONIUM SULPHATE AND MONOCALCIUM PHOSPHATE ON H-ION CONCENTRATION OF SOIL-FILM WATER

The results heretofore reported in this paper with ammonium sulphate and acid phosphate have been derived from soil suspensions. The question arises, Is the film water of the soil affected in the same or different manner from the free water? To secure data on this question three soils were treated with the ammonium sulphate and monocalcium phosphate at optimum moisture conditions and extractions made with the Morgan apparatus. The materials were applied in solution as a fine spray over the soils in order to get as good distribution as possible. The soils were well worked after the additions to get a uniform mass. Monocalcium phosphate was substituted for acid phosphate on account of its complete solubility. Table VII gives the data derived from treatment with ammonium sulphate.

The film water is shown to be more strongly acid from the treatment with ammonium sulphate than that developed when the same amount of salt is applied in suspension. The indications from this are that methods for estimating soil reaction or lime requirement based on treating the soil with a neutral solution do not give the total acidity in the filtered extract.

The mechanism of this reaction has been the subject of much contention. The explanation which has been offered that the basic radicle has been absorbed by celloidal material; and the acidity developed from the combination of SO_4 with 2H of the slightly ionized H_2O leaves an unbalanced equation. Parker (*10*) contends that the fine soil particles catalyze the reaction $(NH_4)_2SO_4 + 2HOH = 2NH_4OH + H_2SO_4$ with the removal of the entire base from solution by selective adsorption

phenomena. The contention that the base has been removed by combination with the difficultly soluble acids more nearly agrees with the results obtained. The measurements showing the effect of monocalcium phosphate on the H-ion concentration of soil-film water are given in Table VIII.

TABLE VII.—*Effect of ammonium sulphate on the H-ion concentration of soil-film water*

Soil type.	Film water.							Free water.					
	Quantity of soil.	Quantity of ammonium sulphate.	Moisture content, dry basis.	Moisture recovered.	Volume of film water.	Voltmeter readings.	H-ion concentration.	Quantity of soil.	Quantity of ammonium sulphate.	Quantity of water.	Suspension of untreated soil.	Voltmeter readings.	H-ion concentration.
	Lbs.	*Gm.*	*P. ct.*	*P. ct.*	*C. c.*		*Gram-molecules per liter.*	*Gm.*	*Gm.*	*C. c.*	*C. c.*		*Gram-molecules per liter.*
Cecil clay loam	10	10	25	6.0	50	0.523	0.5×10^{-3}	5	0.11	50	50	0.644	0.4×10^{-4}
Do	10	20	25	4.8	50	.518	$.7\times10^{-2}$	5	.22	50	50	.612	$.1\times10^{-4}$
Do	10	30	25	5.4	50	.496	$.1\times10^{-2}$	5	.33	50	50	.591	$.3\times10^{-4}$
Do								5	.....	50	50	.674	$.1\times10^{-5}$
Porter's loam	10	10	25	13.6	50	.532	$.4\times10^{-3}$	5	.11	50	50	.602	$.2\times10^{-4}$
Do	10	20	25	14.1	50	.503	$.1\times10^{-2}$	5	.22	50	50	.588	$.4\times10^{-4}$
Do	10	30	25	11.2	50	.461	$.6\times10^{-2}$	5	.33	50	50	.572	$.8\times10^{-4}$
Do								5	.....	50	50	.686	$.9\times10^{-5}$
Norfolk fine sandy loam	10	10	20	10.6	50	.540	$.2\times10^{-3}$	5	.11	50	50	.584	$.5\times10^{-4}$
Do	10	20	20	11.9	50	.528	$.4\times10^{-3}$	5	.22	50	50	.578	$.6\times10^{-4}$
Do	10	30	20	13.2	50	.509	1.0×10^{-3}	5	.33	50	50	.566	$.1\times10^{-3}$
Do								5	.....	50	50	.670	$.1\times10^{-5}$

TABLE VIII.—*Effect of monocalcium phosphate on the H-ion concentration of soil-film water*

Soil type.	Quantity of soil.	Quantity of monocalcium phosphate.	Moisture content, dry basis.	Moisture recovered.	Volume of film-water.	Voltmeter readings.	H-ion concentration.
	Pounds.	*Gm.*	*Per cent.*	*Per cent.*	*C. c.*		*Gram-molecules per liter.*
Cecil clay loam	10	10	25	7.4	50	0.588	0.4×10^{-4}
Do	10	20	25	6.3	50	.596	$.3\times10^{-4}$
Do	10	30	25	6.1	50	.562	$.3\times10^{-3}$
Porter's loam	10	10	25	11.8	50	.598	$.2\times10^{-4}$
Do	10	20	25	10.9	50	.602	$.2\times10^{-4}$
Do	10	30	25	14.4	50	.562	$.1\times10^{-3}$
Norfolk fine sandy loam	10	10	20	12.2	50	.602	$.2\times10^{-4}$
Do	10	20	20	11.1	50	.591	$.3\times10^{-4}$
Do	10	30	20	11.9	50	.588	$.4\times10^{-4}$

By comparing the data of Table II with those derived from this experiment it is apparent that only excessive applications of monocalcium phosphate have increased the H-ion concentration. The 20-gm. applications of the salt do not show any increase in "true acidity" with any soil used. The clay loam and loam give a higher H-ion concentration

with the 30-gm. addition. The fine sandy loam shows more "true acidity" with a 20-gm. application than when 10 gm. are added, and still more when 30 gm. have been applied.

The fixation or removal from solution of phosphates is supposed to be done by the bases, such as iron, aluminum, calcium, etc., in the soil. The clay loam and loam soils are well supplied with very fine particles of iron and aluminum compounds. They therefore have the capacity of fixing more soluble phosphate than the fine sandy loam, which has a relatively low content of bases. These data are in accord with those obtained by Conner on soils of Indiana.

SUMMARY

The hydrogen electrode has been used for indicating soil reaction on a number of untreated soils in suspension. The soils experimented with represent a wide range in texture of those common to the area of the southeastern portion of the United States, extending from and including the Appalachian Mountains to the Atlantic Ocean. The H-ion concentration varies from almost "true neutrality" to rather excessive "true acidity" in the soils.

With the Morgan apparatus for extracting film water from soils, it is shown that its reaction is the same as the free water, differing only in intensity.

The effects of certain fertilizers on the H-ion concentration of long-time-treated plots of three soils have been measured, with the following results: (1) Ammonia sulphate has materially increased the H-ion concentration of all plots which have received applications of this material. The acidity thus developed extends often to the subsoil. (2) Sodium nitrate has slightly reduced the acidity of the plots to which it has been applied. (3) Potassium sulphate increases the "true acidity" when applied to soils, though not as greatly as ammonium sulphate. (4) Acid phosphate does not appear to have affected in either direction the H-ion concentrations of field soils. (5) Lime materially increases the OH-ion concentration of field plots to which it has been added.

The acidity developed from ammonium sulphate is more intense in the film than in the free water of three soils.

Monocalcium phosphate does not change in any way the soil-film water until excessive amounts are added.

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